

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 620 482 A122278 U.S. PTO
10/758577

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **93201073.9**(51) Int. Cl.⁵: **G03C 5/16, G03C 1/30,
G03C 1/38, G03C 5/305,
G03C 11/16**(22) Date of filing: **13.04.93**(43) Date of publication of application:
19.10.94 Bulletin 94/42(84) Designated Contracting States:
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B-2640 Mortsel (BE)**(54) **Method of processing forehardened silver halide photographic industrial X-ray films.**

(57) In accordance with this invention a method is provided of image forming by the steps of exposing a silver halide industrial X-ray photographic material and processing said material in an automatic processing machine in hardener-free developing and hardener-free fixing solutions followed by rinsing and drying with infrared drying means in the film-drying station and wherein said material comprises a support and on at least one side thereof at least one gelatino silver halide emulsion layer and at least one non-sensitive protective antistress coating which optionally comprises at least one polyoxyalkylene compound, the total amount of silver halide per square meter and per side corresponding to 6 to 20 g of silver nitrate, and that said material has been hardened with at least one vinyl sulphone compound thereby reducing the amount of water absorption of the processed film just before drying to less than 2.5 g of water per gram of coated gelatin. Moreover improved physical surface characteristics can be obtained if in addition a polyoxyalkylene compound is added to at least one of the hydrophilic layers of the photographic material and/or if during the processing of the said material in an automatic processing machine the hardener-free developer comprises as a surfactant at least one anionic alkylphenoxy and/or alkoxy polyalkyleneoxy phosphate ester, sulphate ester, alkyl carboxylic, sulphonic or phosphonic acid and/or a salt thereof.

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1. Field of the invention.

This invention relates to a method of providing an image on a silver halide photographic industrial X-ray film by image-wise exposure followed by processing in automatic processing machines filled with hardener free chemicals and having infrared drying means in the drying station.

2. Background of the invention

For industrial radiography a normal processing cycle is characterised by the following steps: developing at 28°C and fixing at 26°C, rinsing and drying. The developer is normally composed from three concentrates that should be diluted in the right order: alkaline solution A contains hydroquinone, acidic solution B contains 1-phenyl-3-pyrazolidinone and acidic solution C contains glutaric dialdehyd as hardening agent. The need for the complex three-part packaged developer concentrates has been dictated by the fact that glutaric aldehyd tends to react with 1-phenyl-3-pyrazolidinone, that this pyrazolidinone is unstable in alkaline medium and that glutaric aldehyd tends to polymerize in alkaline medium. The fixer is composed from 2 concentrated solutions, whereby solution A contains the commonly used highly active ammonium thiosulphate as a fixing agent and solution B contains aluminum sulphate as a hardening agent. Hardening agents are necessary to lead the film through the processor without damages, to reduce the amount of water absorption and, as a consequence, to reduce the drying time and to enhance the drying capacity. This is especially important for industrial X-ray films as these films are coated with a high amount of gelatin e.g. about 30 g/m². The said high amount of gelatin is a consequence of the need to have high coated amounts of silver halide crystals capable of absorbing direct X-rays in industrial X-ray applications.

Damages of the film in the processor are e.g. due to sticking phenomena which may occur due to an inadequate drying method. The drying process can be improved by the use of e.g. infrared dryers.

From an ecological and an economical point of view, it would be important to depart from the concept of hardener containing processing solutions and to work more customer-friendly.

By omitting the toxicologically questionable glutaric dialdehyd from the developer and the aluminum sulphate from the fixer one-part package chemistry could be offered to the customer. From an environmental point of view specific advantages resulting therefrom would be a reduction in package waste and a customer-friendly treatment which doesn't require the preparation of a mixture of two or three different parts before starting the processing cycle.

Besides the presence of less products and less packaging to be handled, the total cost for the customer would decrease, which may be considered as a significant economical advantage. Last but not least the real advantages would occur in the automatic processors, such as less crystal formation on the rollers and less sludge in the processing solutions resulting in less dust on the film surface.

However the introduction of hardener-free processing chemistry, makes the drying capacity in the processor decrease, even when infrared dryers are applied and when the film is to be hardened with formaldehyd as a well-known and frequently used hardening agent. Sticking phenomena of the film at the transport rollers result in a distortion of the images, making them unavailable for diagnostic purposes like examinations of welded seams for applications as e.g. pipe-lines, wherefor image quality, especially detail rendering, has to be excellent.

3. Objects of the invention.

It is an object of the present invention to provide an image forming method by processing an industrial X-ray film with hardener-free processing chemicals in automatic processing machines having infrared drying means in the drying station wherein drying is improved.

Related therewith it is another object to provide a film showing improved physical surface characteristics so that during said processing no damage occurs of the surface of said film due to sticking and as a consequence thereof the obtained image has an enhanced diagnostic value.

Further objects will become apparent from the description hereinafter.

4. Summary of the invention.

In accordance with this invention a method is provided of image forming by the steps of exposing a silver halide industrial X-ray photographic material and processing said material in an automatic processing machine in hardener-free developing and hardener-free fixing solutions followed by rinsing and drying with infrared drying means in the film-drying station characterised in that said material comprises a support and

on at least one side thereof at least one gelatin silver halide emulsion layer and at least one non-sensitive protective antistress coating, the total amount of silver halide per square meter and per side corresponding to 6 to 20 g of silver nitrate, and that said material has been hardened with at least one vinyl sulphone compound thereby reducing the amount of water absorption of the processed film just before drying to less than 2.5 g of water per gram of coated gelatin. Moreover improved physical surface characteristics can be obtained if in addition a polyoxyalkylene compound is added to at least one of the hydrophilic layers of the photographic material and/or if during the processing of the said material in an automatic processing machine the hardener-free developer comprises as a surfactant at least one anionic alkylphenoxy and/or alkoxy polyalkyleneoxy phosphate ester, sulphate ester, alkyl carboxylic, sulphonic or phosphonic acid and/or a salt thereof.

5. Detailed description of the invention.

According to the present invention the gelatin binder of the silver halide photographic industrial X-ray elements is hardened with hardening agents of the vinylsulphone type. Especially di-(vinyl-sulphonyl)-methane and ethylene di-vinyl-sulphone are preferred. As opposed to the appropriate aldehyde type hardeners, like e.g. formaldehyde, vinylsulphone type hardeners used to harden industrial X-ray materials don't show disadvantageous sticking phenomena between the film and the rollers in the drying section of automatic processor with infrared dryers as drying means in that section of the automatic processing unit.

The hardening agent may be added to the coating composition of the emulsion layer(s) and/or to the coating composition of the protective antistress layer(s) before or during the coating procedure. If the hardener is added during the coating procedure it is still possible to make corrections for the water absorption of the material that has to be coated, by controlling the amount of water absorption for the already coated material directly after coating.

Hardening is preferably provided to such an extent that, when the photographic material is rinsed at the end of the processing cycle just before drying, an amount of less than 2.5 grams of water per gram of coated gelatin is absorbed.

In accordance with this invention the silver halide emulsions coated in the silver halide emulsion layer(s) comprise silver chloride, silver chlorobromide, silver chlorobromiodide, silver bromide or silver bromiodide. Suitable silver chloride and silver chlorobromide emulsions have e.g. been described in EP-Application No. 91202761.2, filed October 24, 1991.

Preferred are silver bromiodide emulsions comprising at most 10 mole% of iodide, preferably at most 3 mole% and still more preferably 1 mole%. It is preferred to use regular-shaped silver halide crystals and more particularly silver bromiodide emulsions with cubic crystal habit which are commonly used in industrial radiographic materials and are known to have good development characteristics with respect to high sensitivity. During the precipitation stage of the emulsion making the parameter determining whether cubic or octahedral crystals are formed is the pAg of the solution.

The pAg of the solution may be regulated by any of the means known in the art of emulsion making, such as the electronic control apparatus and method disclosed in U.S. Patent 3,821,002.

From the article "Der Einfluß der Wachstumsbedingungen auf die Kristalltracht der Silberhalogenide" (the influence of Growth Conditions on the Crystalline Behaviour of Silver halides) von E. Moisar and E. Klein, Bunsengesellschaft für physikalische Chemie, Berichte 67 949-957 (1963) No 9.10., it is known that on allowing tetradecahedral crystals of a homodisperse silver bromide emulsion to grow by controlled addition of solutions of silver nitrate and potassium bromide, crystals of cubic form are obtained under conditions of low excess bromide concentration in the solution phase. A preferred embodiment of making the emulsions used according to the present invention involves the preparation of high-sensitive silver bromiodide emulsions as these X-ray emulsions, by precipitation under double jet conditions. Although nowadays processes for the preparation of homogeneous silver halide emulsions make use of special control devices to regulate the form of the resulting silver halide crystals, said form mainly being determined by the pAg value and temperature in the reaction vessel, the silver ion concentration can be kept constant during the precipitation by the use of a special inlet technique as described in Research Disclosure 10308.

The average grain-size of the silver halide emulsions made according to the present invention is preferably situated between 0.1 and 1.0 μm . Particle size of silver halide grains can be determined using conventional techniques e.g. as described by Trivelli and M. Smith, The Photographic Journal, vol. 69, 1939, p. 330-338, Loveland "ASTM symposium on light microscopy" 1953, p. 94-122 and Mees and James "The Theory of the photographic process" (1977), Chapter II.

To obtain a reproducible crystal size especially the flow rate and concentration of the solutions, the temperature and pAg have to be adjusted very carefully. Grain-growth restrainers or accelerators may be

added from the start or during the preparation of the emulsion crystals. Depending on the initial conditions during precipitation, monodispersed emulsions can be prepared as is preferred for this invention. Monodispersed emulsions in contrast to heterodispersed emulsions have been characterized in the art as emulsions of which at least 95 % by weight or number of the grains have a diameter which is within about 40 %, preferably within about 30 % of the mean grain-diameter and more preferably within about 10% to 20%.

Silver halide grains having a very narrow grain-size distribution can thus be obtained by strictly controlling the conditions at which the silver halide grains are prepared using a double jet procedure. In such a procedure, the silver halide grains are prepared by simultaneously running an aqueous solution of a water-soluble silver salt for example, silver nitrate, and water-soluble halide, for example, a mixture of potassium bromide and potassium iodide, into a rapidly agitated aqueous solution of a silver halide peptizer, preferably gelatin, a gelatin derivative or some other protein peptizer. Even colloidal silica may be used as a protective colloid as has been described in EP Application 392,092.

In a preferred embodiment the rates of addition of the silver nitrate and halide salt solutions are steadily increased in such a way that no renucleation appears in the reaction vessel. This procedure is especially recommended, not only to save time but also to avoid physical ripening of the silver halide crystals during precipitation, the so-called Ostwald ripening phenomenon, which gives rise to the broadening of the silver halide crystal distribution.

Once the grains have reached their ultimate size and shape, the emulsions are generally washed after being flocculated to remove the by-products of grainformation and grain-growth. In order to remove the excess of soluble salts washing is applied at a pH value which can vary during washing but remains comprised between 3.7 and 3.0 making use of a flocculating agent like polystyrene sulphonic acid. The emulsion may be washed by diafiltration by means of a semipermeable membrane, also called ultrafiltration, so that it is not necessary to use polymeric flocculating agents that may disturb the coating composition stability before, during or after the coating procedure. Such procedures are disclosed e.g. in Research Disclosure Vol. 102, Oct. 1972, Item 10208, Research Disclosure Vol. 131, March, Item 13122 and Mignot US-Patent 4,334,012. Preferably, at the start of the ultrafiltration, there is no pH and pAg adjustment as pH and pAg are maintained at the same level as at the end of the preceding precipitation without any adjustment stage.

In accordance with the present invention, the emulsions are preferably washed by acid-coagulation techniques using acid-coagulable gelatin derivatives or anionic polymeric compounds or, when precipitation occurred in silica medium, by certain polymers capable of forming hydrogen bridges with silica, in an amount sufficient to form coagulable aggregates with the silica particles as has been described in EP Application 517 961.

Coagulation techniques using acid-coagulable gelatin derivatives have been described e.g. in U.S. Patent Specifications 2,614,928, 2,614,929 and 2,728,662. The acid-coagulable gelatin derivatives are reaction products of gelatin with organic carboxylic or sulphonic acid chlorides, carboxylic acid anhydrides, aromatic isocyanates or 1,4-diketones. The use of these acid-coagulable gelatin derivatives generally comprises precipitating the silver halide grains in an aqueous solution of the acid coagulable gelatin derivative or in an aqueous solution of gelatin to which an acid coagulable gelatin derivative has been added in sufficient proportion to impart acid-coagulable properties to the entire mass. Alternatively, the gelatin derivative may be added after the stage of emulsification in normal gelatin, and even after the physical ripening stage, provided it is added in an amount sufficient to render the whole coagulable under acid conditions. Examples of acid-coagulable gelatin derivatives suitable for use in accordance with the present invention can be found e.g. in the United States Patent Specifications referred to above. Particularly suitable are phthaloyl gelatin and N-phenylcarbamoyl gelatin.

The coagulum formed may be removed from the liquid by any suitable means, for example the supernatant liquid is decanted or removed by means of a siphon, where upon the coagulum is washed out once or several times.

Washing of the coagulum may occur by rinsing with mere cold water. However, the first wash water is preferably acidified to lower the pH of the water to the pH of the coagulation point. Anionic polymer e.g. polystyrene sulphonic acid may be added to the wash water even when an acid coagulable gelatin derivative has been used e.g. as described in published German Patent Specification (DOS) 2,337,172 mentioned hereinbefore. Alternatively washing may be effected by redispersing the coagulum in water at elevated temperature using a small amount of alkali, e.g. sodium or ammonium hydroxide, recoagulating by addition of an acid to reduce the pH to the coagulation point and subsequently removing the supernatant liquid. This redispersion and recoagulation operation may be repeated as many times as is necessary.

After the washing operation, the coagulum is redispersed to form a photographic emulsion suitable for the subsequent finishing and coating operations by treating, preferably at a temperature within the range of 35 to 70 °C, with the required quantity of water, gelatin and, if necessary, alkali for a time sufficient to effect a complete redispersal of the coagulum.

5 Instead or in addition to normal gelatin, which is preferably used, other known photographic hydrophilic colloids can also be used for redispersion e.g. a gelatin derivative as referred to above, albumin, agar-agar, sodium alginate, hydrolysed cellulose esters, polyvinyl alcohol, hydrophilic polyvinyl copolymers, colloidal silica etc.

The light-sensitive silver halide emulsions are chemically sensitized with a sulphur and gold sensitizer. 10 This can be done as described i.a. in "Chimie et Physique Photographique" by P. Glafkides, in "Photographic Emulsion Chemistry" by G.F. Duffin, in "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in said literature sulphur sensitization can be carried out by effecting the ripening in the presence of small amounts of compounds 15 containing sulphur e.g. thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodamines. Gold sensitization occurs by means of gold compounds. In addition small amounts of compounds of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd or Pt can be used. The emulsion can be sensitized in addition by means of reductors e.g. tin compounds as described in GB-A 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds.

20 If more than one silver halide emulsion is used in one or more emulsion layers, the said halide emulsions are chemically ripened separately.

As has been set forth in EP-Application No. 92200420.5 filed on February 14, 1992 the image tone can be improved by making mixtures of chemically ripened cubic monodisperse silver bromoiodide crystals and chemically ripened cubic monodisperse silver chloride and/or silver chlorobromide and/or silver 25 chlorobromoiodide emulsion crystals, wherein the added non-silver bromoiodide crystals have also been ripened separately.

In accordance with the present invention compounds for preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of photographic elements or during the photographic treatment thereof may be supplementary added. Examples of such stabilizers are heterocyclic 30 nitrogen-containing stabilizing compounds as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline-thione, triazaindenes, tetrazaindenes and pentazain- 35 denes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB-A 1,203,757, GB-A 1,209,146, JA-Appl. 75-39537, and GB-A 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US Patent 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid, benzenethiosulphonic acid amide and other disulfide derivatives, which are giving an unsatisfactory result if added as the sole stabilizing agent and are therefore 40 combined with other stabilizers belonging to the classes of stabilizers already mentioned. On the other hand mercury salts and other metal-salts that can be used as fog-inhibiting compounds such as cadmium salts and related compounds described in Research Disclosure N° 17643 (1978), Chapter VI, should be avoided for reasons of ecology.

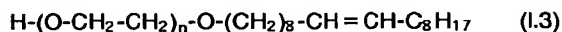
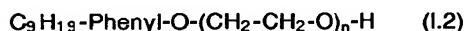
The weight ratio of gelatin to silver halide (expressed as silver nitrate) in the silver halide emulsion 45 layers of the photographic material according to the present invention is comprised between 0.3 and 1.2, preferably between 0.6 and 1.1.

For industrial radiography the silver halide emulsion layer(s) comprise total amounts of silver halide, coated per side and per square meter of from 6 to 20 g, expressed as the equivalent amounts of silver nitrate.

50 The photographic elements under consideration may further comprise various kinds of surface-active agents in the photographic emulsion layer and/or in at least one other hydrophilic colloid layer. It has been stated in a preferred embodiment that if one or more polyoxyalkylene compound(s) are simultaneously present as surfactants dust at the film surface after processing disappears to an acceptable level for materials with such a high silver content as silver halide industrial X-ray photographic films as has been 55 mentioned hereinbefore. Said total amounts evidently promote the appearance of dust.

A preferred polyoxyalkylene compound reducing dust to an acceptable level is the condensation product of castor oil and polyethylene oxide with about 40 recurrent units, the formula (I.1) of which is given hereinafter. The said at least one polyoxyalkylene compound is preferably present in an amount between 10

to 200 mg per square meter and per side of the film support and still more preferably in an amount between 20 to 100 mg per square meter and per side of the film support. Preferred compounds of this type are



Compounds (I.1) to (I.4) preferably have molecular weights from 300 to about 4000.

Both the polyoxyalkylene compound(s) and the hardener(s) described hereinbefore are preferably present in at least one of the non light-sensitive layers and more preferably both compounds are added to the protective antistress layer which is preferably present as an outermost layer at both sides of the support.

Other preferred surface-active coating agents are compounds containing perfluorinated alkyl groups. Other suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides e.g. polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, siliconepolyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agents comprising an acid group such as a carboxy, sulphy, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Such surface-active agents can be used for various purposes e.g. as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion, and as compounds improving the photographic characteristics e.g. higher contrast, sensitization, and development acceleration.

Development acceleration can be accomplished with the aid of various compounds, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-A 3,038,805 - 4,038,075 - 4,292,400.

35 The photographic elements may further comprise various other additives such as e.g. compounds improving the dimensional stability of the photographic element, UV-absorbers, spacing agents and plasticizers.

Suitable additives for improving the dimensional stability of the photographic element are i.a. dispersions of a water-soluble or hardly soluble synthetic polymer e.g. polymers of alkyl (meth)acrylates, alkoxy-(meth)acrylates, glycidyl (meth)acrylates, (meth)acrylamides, vinyl esters, acrylonitriles, olefins, and styrenes, or copolymers of the above with acrylic acids, methacrylic acids, Alpha-Beta-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphonyl (meth)acrylates, and styrene sulphonic acids.

Suitable UV-absorbers are i.a. aryl-substituted benzotriazole compounds as described in US-A 3,533,794, 4-thiazolidone compounds as described in US-A 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-A 3,705,805 and 3,707,375, butadiene compounds as described in US-A 4,045,229, and benzoxazole compounds as described in US-A 3,700,455.

In general, the average particle size of spacing agents is comprised between 0.2 and 10 μm . Spacing agents can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents usually are removed therefrom in an alkaline processing bath. Suitable spacing agents can be made i.a. of polymethyl methacrylate, of copolymers of acrylic acid and methyl methacrylate, and of hydroxypropylmethyl cellulose hexahydrophthalate. Other suitable spacing agents have been described in US-A 4,614,708.

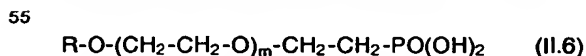
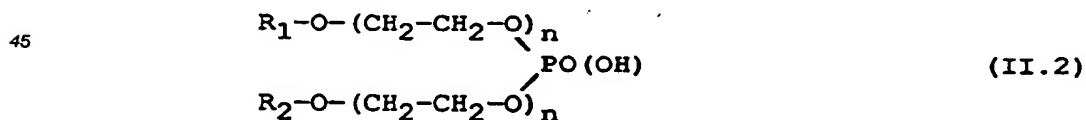
The photographic element can comprise an antistatic layer e.g. to avoid static discharges during coating, processing and other handlings of the material. Such antistatic layer can be an outermost coating or stratum of one or more antistatic agents or a coating applied directly to the film support. Said antistatic layer(s) may be overcoated with a barrier layer of e.g. gelatin. Antistatic compounds suitable for use in such layers are e.g. vanadium pentoxide sols, tin oxide sols or conductive polymers such as polyethylene oxides,

The support of the photographic material in accordance with the present invention may be a transparent resin, preferably a blue coloured polyester support like polyethylene terephthalate. The thickness of such organic resin film is preferably about 175 μm . The support is provided with a substrate layer at both sides to have good adhesion properties between the emulsion layer and said support.

The photographic industrial X-ray material can be image-wise exposed by means of an X-ray radiation source the energy of which, expressed in kV, depends on the specific application. Another typical radiation source is a radioactive Co^{60} source. To reduce the effect of scattering radiation a metal screen, usually a lead screen, is used in combination with the photographic film. Besides the generation of secondary electrons makes the sensitivity to enhance.

The developer solution according to the invention has to be replenished not only for decrease of the liquid volume due to cross-over into the next processing solution but also for pH-changes due to oxidation of the developer molecules. This can be done on a regular time interval basis or on the basis of the amount of processed film or on a combination of both. The development step can be followed by a washing step, a fixing solution and another washing or stabilization step. Finally after the last washing step the photographic material is dried by means of infrared drying means as cited hereinbefore.

A further improvement consists in measures in the processing of the materials described hereinbefore in automatical processing machines wherein the developer solution comprises as a surfactant at least one anionic alkyl-phenoxy and/or alkoxy polyalkyleneoxy phosphate ester (compounds II.1 and II.2), sulphate 35 ester (compound II.3), alkyl carboxylic, sulphonic or phosphonic acid (compounds II.4, II.5 and II.6 respectively) and/or a salt thereof. Preferably the said at least one anionic alkylphenoxy polyalkyleneoxy phosphate ester surfactant present in the developer solution is an alkyl-phenoxy-(ethyleneoxy)_n phosphoric acid mono- or di-ester compound or a mixture thereof (see compounds (II.1) and (II.2)) in their salt form, 40 wherein n is a positive integer of at least 4 and the alkyl group is a C₈ to C₂₀ alkyl group.



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a substituted or unsubstituted alkyl-group
or R₃-Phenyl or R₄-Phenyl

and wherein each of R₃ and R₄ independently represent an alkyl group, preferably C₈-C₂₀ alkyl, m and n are integers from about 3, respectively 4, to about 30.

Preferred amounts of the said at least one ionic surfactant present in the developer are from about 25 to 200 mg/l.

The processing of the exposed materials, characterised by the steps of developing and fixing wherein the developer preferably comprises at least one of the compounds (II.1) or (II.2) as described hereinbefore may thus be performed with the hardener-free solutions according to this invention.

The developer solution according to the invention has further to be replenished not only for decrease of the liquid volume due to cross-over into the next processing solution but also for pH-changes due to oxidation of the developer molecules. This can be done on a regular time interval basis or on the basis of the amount of processed film or on a combination of both. The development step can be followed by a washing step, is further followed by a fixing solution and further by another washing or stabilization step. As in the hardener-free fixing solution aluminum sulphate is omitted, the disappearance of the deposit of aluminum salts at the rollers in the fixation zone of the automatic processor further leads to an improvement of the surface characteristics of the processed film material. No more transfer can thus be observed of said deposit from the rollers to the film and vice versa resulting in dust deposit on the film surface.

As a consequence extra physical means to remove dust from the film surface as e.g. brush rollers present in the processor (like hitherto for the STRUCTURIX NDT-3 machine, trade name marketed by Agfa-Gevaert and for the EK-Mod.B, trade name marketed by Eastman Kodak) after the rinsing unit following fixation may be omitted. For the customer this leads to a lower cost price as he also needs less support.

Of course processing conditions and composition of processing solutions are dependent from the specific type of photographic material. For example, according to this invention for materials for industrial X-ray diagnostic purposes an automatically operating processing apparatus is used provided with a system for automatic regeneration of the processing solutions. The forehardened material may be processed using one-part package chemistry or three-part package chemistry, but it is clear that if one-part package chemistry can be applied it will be preferred as it is more customer-friendly, omitting the mixing procedures of solutions. Applications within total processing times of 90 seconds are possible. From an ecological point of view it is even possible to use sodium thiosulphate instead of ammonium thiosulphate in the fixer.

It is clear that the improvements stated for industrial X-ray films will also apply to X-ray medical films of high silver halide content.

The following examples illustrate the invention without however limiting it thereto.

6. Examples

Example No. 1.

A gelatino silver iodobromide X-ray emulsion comprising 99 mole % of silver bromide and 1 mole % of silver iodide was prepared in the following way. An aqueous solution containing 3 grams of ammonia was added to the reaction vessel containing 1550 ml of a 3 % by weight aqueous solution of gelatin at 45 °C. Into said reaction vessel a solution of 2000 ml of an aqueous 1.5 molar solution of potassium bromide and a solution of 2000 ml of an aqueous 1.5 molar solution of silver nitrate were introduced at constant rate of 86 ml/min under vigorously stirring conditions. During precipitation the pAg value was adjusted to and maintained at a value corresponding to an E.M.F. of +20 mV with reference to a silver/saturated calomel electrode. In this way homogeneous and regular silver halide grains having a crystal diameter of 0.54 µm were obtained.

At the end of the precipitation step, the emulsion was coagulated by adding polystyrene sulphonic acid acting as a flocculating agent after adjustment of the pH value of the emulsion in the reaction vessel to 3.5 with sulphuric acid. After rapid sedimentation of said silver halide emulsion the supernatant liquid was decanted. To remove the water-soluble salts from said flocculate, demineralized water of 11 °C was added under controlled stirring conditions followed by a further sedimentation and decantation. This washing procedure was repeated until the emulsion was sufficiently desalted. Thereafter the coagulum was redispersed at 45 °C in water after the addition of a sufficient amount of gelatin to obtain a ratio of gelatin to silver halide expressed as silver nitrate of 0.4. The pH-value was adjusted to 6.5 and pAg to a value of +70 mV with reference to the silver/saturated calomel electrode.

Chemical sensitization of said emulsion was performed by the addition of a sulphur and gold sensitizer and digestion at 50 °C to the point where the highest sensitivity was reached for a still acceptable fog level.

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This emulsion was coated at both sides of a blue polyethylene terephthalate support having a thickness of 175 μm , so that per sq. m. an amount of silver halide corresponding to 14.5 g of silver nitrate and 12.3 g of gelatin were present. Before coating stabilizers such as 5-methyl-7-hydroxy-5-triazolo-[1,5-a]-pyrimidin and 1-phenyl-5-mercaptotetrazol were added to the emulsion.

5 From the samples of the materials thus formed, the emulsion layers were covered at both sides with a protective layer of 1.5 grams of gelatin per square meter, which were hardened with 0.066 g of formaldehyd (FMD) per square meter for the comparative material No. 2 and with 0.093 g of di-(vinyl-sulphonyl)-methane (DVS) per square meter for the material No. 1 as set forth in Table 1.

10 The coated and dried films were exposed according to ISO 7004 with a 235 kV radiation source with a copper filter of 8 mm thickness.

The exposed radiographic films were developed, fixed, rinsed and dried in an automatic machine processing cycle of 8 minutes. The film was run in a Structurix NDT-1 machine marketed by Agfa-Gevaert and developed at 28 °C in a one-part package developer, followed by fixation in a one-part package fixer as described hereinafter.

15 In the drying section infrared drying means were present. It was possible to make an evaluation of the surface state of the processed film at 8 drying levels.

The composition of the concentrated one-part package developer (amounts given in grams/liter) is as follows:

20	water	200 ml
	potassium bromide	6 grams
	potassium sulphite (65% solution)	247 grams
	ethylenediamine tetraacetic acid, tetrasodium salt trihydrate	9.6 grams
25	hydroquinone	112.0 grams
	5-methylbenzotriazole	0.076 grams
	1-phenyl-5-mercaptotetrazole	0.040 grams
	sodium tetraborate (decahydrate)	18.0 grams
	potassium carbonate	38.0 grams
30	potassium hydroxyde	42.0 grams
	diethylene glycol	100.0 grams
	potassium iodide	0.088 grams
	4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone	12.0 grams
35	Water to make 1 liter. pH adjusted to 11.15 at 25 °C with potassium hydroxide.	

For initiation of the processing one part of the concentrated developer was mixed with 3 parts of water. No starter was added. The pH of the mixture was 10.40 at 25 °C.

40 The composition of the concentrated one-part package fixer:

45	ammoniumthiosulphate (59% solution)	552 grams
	boric acid	20.8 grams
	sodium sulphite	45 grams
	sodium acetate.3 aq	58 grams
	sulphuric acid (99% solution)	48.5 ml
50	Water to make 1 liter. pH adjusted to 4.80 at 25 °C with sulphuric acid.	

For initiation of the processing 1 part of the concentrated fixer was mixed with 4 parts of water. The pH of this mixture was 4.73 at 25 °C.

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Tabel 1

Evaluation of the drying velocity and sticking phenomena observed at the surface of the films in automatic processors filled with one part-package hardener-free chemistry (composition as described hereinbefore).								
Dryer level Emulsion No.	2	3	4	5	6	7	8	9
1 (invention)	0	0	0	0	0	0	0	0
2 (comp.)	WET	WET	*	*	*	*	*	*

For both materials, the material according to the invention (1) and the comparative material (2) the amount of water absorption per square meter is 59 g.

As can be seen from table 1 the material hardened with di-(vinyl-sulphonyl)-methane (emulsion No. 1 as inventive example) is dried more quickly: already at dryer level 2, the drying characteristics are satisfying, as is indicated by evaluation mark "0", without giving rise to sticking. For the comparative example, hardened with formaldehyd, at different dryer levels problems are met with sticking at the first roller pair, leading to jamming or wrapping around it. The occurrence of such undesirable effects is indicated with (*).

Example No. 2.

A gelatino silver iodobromide X-ray emulsion comprising 99 mole % of silver bromide and 1 mole % of silver iodide was prepared having a mean crystal diameter of 0.2 μm and a cubic habit.

Chemical sensitization of said emulsion was performed by the addition of a sulphur and gold sensitizer and digestion at 50 °C to the point where the highest sensitivity was reached for a still acceptable fog level.

This emulsion was coated at both sides of a blue polyethylene terephthalate support having a thickness of 175 μm , so that per sq. m. an amount of silver halide corresponding to 10.0 g of silver nitrate and 8.5 g of gelatin were present. Before coating stabilizers such as 5-methyl-7-hydroxy-5-triazolo-[1,5-a]-pyrimidin and 1-phenyl-5-mercaptotetrazol were added to the emulsion. From the samples of the materials thus formed, the emulsion layers were covered at both sides with a protective layer of 1.5 grams of gelatin per square meter, which were hardened with 0.195 g of di-(vinyl-sulfonyl)-methane (DVS) per square meter for the materials Nos. 1 and 2 as set forth in Table 2.

The protective layers at both sides of the film support of material No. 2 additionally contained a polyoxyalkylene compound (indicated as POAC in the Table 2) corresponding to the formula (I.1) in an amount of 0.042g/m² the film. The coated and dried films were exposed according to ISO 7004 with a 235 kV radiation source with a copper filter of 8 mm thickness.

The exposed radiographic films were developed, fixed, rinsed and dried in an automatic machine processing cycle of 8 minutes. In experiment No. 1 development occurred in hardening containing developer G135 (trade name) marketed by Agfa-Gevaert, at 28 °C further called DEV, which comprised hydroquinone, phenidone, potassium sulphite, 1-phenyl-5-mercaptotetrazole, 5-nitroindazole and glutaric dialdehyde. In the same experiment No. 1 fixing occurred in a hardener containing fixer G335 (trade name) marketed by Agfa-Gevaert, at 28 °C, hereinafter called FIX, which comprised aluminum sulphate, sodium sulphite, boric acid and sodium acetate.

In experiment No. 2 the same material No. 1 was processed in hardener-free processing solutions made from the one-part package concentrated developer and the one-part package concentrated fixer as in example No. 1 given hereinbefore.

The hardener-free solutions of the developer and of the fixer are further called HFDEV and HFFIX respectively.

In addition, if compound (II.1) was added to the developer as an anionic alkylphenoxy polyalkyleneoxy phosphate ester surfactant, in an amount of 100 mg/liter, said developer was called HFDEVPHOS.

In Table 2 shown hereinafter the combinations are summarized of developers and fixers wherein the materials Nos. 1 and 2, exposed as described hereinbefore, were run.

To simulate severe real circumstances that might initiate dust on the film surface after processing of the materials the following procedure was performed:

- an amount of film was exposed to such an extent as to have a moderate density corresponding to the practically obtained average density for real samples after processing. The said amount of film was run through the processor to cause a replenishment of the processing solutions so that the said

processing solutions were totally regenerated. In praxis about 10 m² per day were run through the said processing solutions and the applied regeneration was 900 ml/m² for the developer and 1200 ml/m² for the fixer. For every experimental combination of film and processing solutions as summarized in Table 2, this procedure was started up again to reach good working conditions wherein appearance of dust at the surface could be evaluated.

Therefor after the said working conditions were reached unexposed sheets of the different materials were run through the processor. The first ten sheets of each material were examined superposed to make an objective evaluation possible.

Figures ranging from 0 to 3 were given with the following significance for the appearance of dust at the film surface after processing:

3 or 2: acceptable dust-level for non-critical customers

1: acceptable dust-level for critical customers

0: no visibly detectable dust

In Table 2 these figures are corresponding with the comments just given hereinbefore.

Table 2

Material No.	Developer	Fixer	Dust level	Exp.
1 DVS	DEV	FIX	2	1
1 DVS	HFDEV	HFFIX	3	2
2 DVS/POAC	HFDEV	HFFIX	1-2	3
2 DVS/POAC	HFDEVPHOS	HFFIX	0-1	4

As can be seen from Table 2 also in hardener free chemicals the dust level at the film surface after processing is reduced to an acceptable level, especially if the materials that have been processed in hardener-free processing solutions comprise at least one polyoxyalkylene compound as a surfactant in the protective coating layer. A further improvement is obtained if in the hardener free developer an anionic alkylphenoxy polyalkyleneoxy phosphate ester surfactant is present as is clearly illustrated by experiment No. 4.

Claims

- Method of image forming by the steps of exposing a silver halide industrial X-ray photographic material and processing said material in an automatic processing machine in hardener-free developing and hardener-free fixing solutions followed by rinsing and drying with infrared drying means in the film-drying station characterised in that said material comprises a support and on at least one side thereof at least one gelatino silver halide emulsion layer and at least one non-sensitive protective antistress coating, the total amount of silver halide per square meter and per side corresponding to 6 to 20 g of silver nitrate, and that said material has been hardened with at least one vinyl sulphone compound thereby reducing the amount of water absorption of the processed film just before drying to less than 2.5 g of water per gram of coated gelatin.
- Method according to claim 1, wherein the vinyl sulphone hardener is di-(vinyl-sulphonyl)-methane or ethylene di-(vinyl-sulphone).
- Method according to claim 1 or 2, wherein in the said material at least one polyoxyalkylene compound is present as a surfactant in at least one of its hydrophilic layers.
- Method according to claim 3, wherein said at least one polyoxyalkylene compound is present in an amount between 10 to 200 mg/m² per side of the film support.
- Method according to claim 3, wherein said at least one polyoxyalkylene compound is present in an amount between 20 to 100 mg/m² per side of the film support.

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6. Method according to any of claims 3 to 5, wherein said at least one polyoxyalkylene compound is the condensation product of castor oil and polyethylene oxide with 40 recurrent units.
- 5 7. Method according to any of claims 3 to 6, wherein said polyoxyalkylene compound(s) is (are) present in a protective antistress coating at both sides of the film support.
8. Method according to any of claims 1 to 7, wherein the hardener-free developing solution comprises as a surfactant at least one anionic alkylphenoxy and/or alkoxy polyalkyleneoxy phosphate ester, sulphate ester, alkyl carboxylic, sulphonic or phosphonic acid and/or a salt thereof.
- 10 9. Method according to claim 8, wherein the said anionic alkylphenoxy polyalkyleneoxy phosphate ester surfactant is an alkylphenoxy-(ethyleneoxy)_n phosphoric acid mono- or di-ester compound in its salt form, wherein n is a positive integer of at least 4 and the alkyl group is a C₈ to C₂₀ alkyl group.
- 15 10. Method of image forming according to claim 8 or 9 wherein the said anionic surfactant is present in the developer in amount of 25 to 200 mg/l.

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EUROPEAN SEARCH REPORT

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-4 990 439 (K.GOAN ET AL.) * column 8, line 12 - column 11, line 34 * * column 13, line 5 - line 14 * * column 16, line 25 - line 35 * * column 18, line 1 - column 19, line 28 * ---	1-10	G03C5/16 G03C1/30 G03C1/38 G03C5/305 G03C11/16
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Y	FR-A-2 367 300 (AGFA-GEVAERT) * page 1, line 1 - line 7 * * page 4, line 5 - line 19 * * page 5, line 15 - line 20 * * page 14, line 14 - page 15, line 9 * * page 18, line 29 - line 32 * * page 19, line 4 - line 37 * * claims 13,14 * ---	1-10	
Y,D	EP-A-0 223 883 (AGFA-GEVAERT) * page 6, line 52 - line 53; claims 1,12,14 * ---	8-10	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
Y	GB-A-805 827 (ILFORD) * claims 1,2 * ---	6	G03C
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 AUGUST 1993	Examiner PHILOSOPH L.
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	

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Y	PATENT ABSTRACTS OF JAPAN vol. 10, no. 338 (P-516)(2394) 15 November 1986 & JP-A-61 140 940 (FUJI PHOTO FILM) 28 June 1986 * abstract * ---	1,2	
Y	PRODUCT LICENSING INDEX no. 95, March 1972, HAVANT GB pages 47 - 48 'Surface-activated rapid drying of hydrophilic layers' item 9518 -----	1,3-10	
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Place of search THE HAGUE		Date of completion of the search 18 AUGUST 1993	Examiner PHILOSOPH L.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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